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Hybrid Matrices Layer of Carbon Fiber Composites

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Abstract

Polymeric composites have gone through a level of maturity beyond the laboratory stage with the development of all composite aircraft structures. Yet the basic understanding of the material used in its primary structure has not been extensively investigated. Although this may be attributed in part to the proprietary nature of the system, we believe that it is because of lack of specific tools required for its analysis. Specifically, micromechanical models always assume an evenly distributed homogeneous matrix while lamination theory assumes constant stress through the laminate thickness. Specifically, this work focuses on the development of model systems that can be studied without concerns of proprietary and/or export control requirements. Consequently, the amount of toughness improvement must be balanced between interlaminar and intralaminar fracture toughness. Finally, this work has demonstrated that even though the multilayer structured laminates provide Mode II interlaminar fracture toughness improvements, their mechanical testing behavior is extremely different than conventional composite structures.

Key words : Laminates, Matrices, Carbon Fiber Composites.

1. INTRODUCTION

Thermosets and thermoplastics are equally considered as possible materials used as matrices for advanced polymeric composite materials. Thermosetting systems are generally more preferable than thermoplastic ones, because the thermoset processing has the advantage of prepreg tack and lower viscosity during the process . Nevertheless, the thermosets used as matrices in polymeric composites were not able to provide the appropriate toughness capabilities in order to fulfill primary structure applications. The need of expand the use of polymeric composites to commercial aircraft primary structures has led to the toughening of thermosetting resin systems as one of the most important objectives and has motivated essential research efforts. Many of those efforts are responsible for the development of a successful toughening technique suitable for primary structure applications that is based on layering concepts to form final multilayer laminate structures. This research focuses on the investigation of the relationship between multilayer structures and various thermosetting matrices in order to produce tougher polymeric composites with layering concepts. Overall, this work provides an understanding on the composite's toughening by the application of layering concepts. When a composite material is tested in impact, the most serious damage that occurs within the laminate structure is ply delamination. Delaminations create great degradation in the resulting composite mechanical properties. Trying to impede delaminations occurred during impact, a successful toughening technique for thermosetting matrix composite systems was developed that has been commercialized and qualified for use in primary structure. This toughening technique establishes an engineering approach to the toughness issue by using layering concepts in order to toughen only the highly stressed interlaminar regions within the composite. Layering is attained by using a tough resin rich layer between the plies of the composite structure which eventually results to a multilayer laminate structure. These layering techniques can be implemented as heterogeneous or homogeneous modification, as schematically presented in Figure 1.

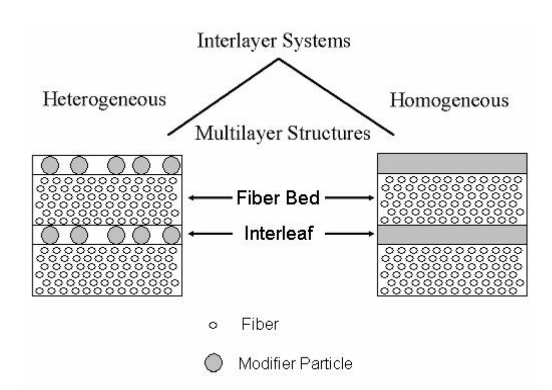


Figure 1: Heterogeneous and Homogeneous Approaches to the Layer Toughening Concept

2.PROCESSING OF MULTILAYER STRUCTURED LAMINATES

The need to exploit the benefits of thermosetting polymer matrix composites in primary commercial airplane structures has led to the development of tougher multilayer thermosetting structures.This work focused on firstly, the

modeling of the interlayer toughening concept with a second rigid modifier particle impregnation phase, hosted in three different resins through the development of a model multilayer composite structure containing a heterogeneous resin interlayer and secondly, with a second pass of resin developing a model multilayer structure containing a homogeneous resin interlayer. In general, the manufacture of conventional high quality composites is consisted of three main steps: prepreg processing, layup and autoclave processing. Trying to get a clear view of the multilayer structured composite process, its development is compared to the development of a conventional structure at each processing step as it is presented in Figure 2.

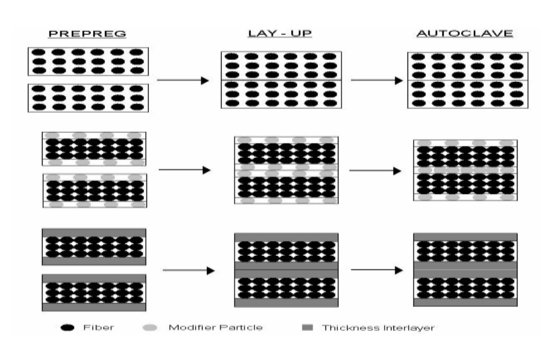


Figure 2: Development of Conventional and Multilayer Structured Composites

2.1 DOUBLE PASS IMPREGNATION

The difference between conventional prepreg and multilayer prepreg structures, either homogeneous or heterogeneous are shown schematically in Figure 2. The conventional prepreg has equally distributed reinforcing fibers within a matrix resin. Ideally, the prepreg has a constant thickness and the fibers have completely been wetted by the matrix resin. On the contrary, multilayer prepreg is generated by using a third component, the interleaf or the interlayer, which must be placed between each ply. Specific packing of the fibers must be performed to the toughened prepreg in order to accumulate the same resin as a conventional prepreg. The tighter fiber packing accumulates less resin between fibers and allows for excess resin to remain on the prepreg surfaces. Acquiring a fully impregnated structure with low resin content within fibers is another difficulty of the prepreg processing. In processing of this multilayer prepreg structure, different techniques can be used depending on the kind of multilayer (heterogeneous or homogeneous).

2.1.1 Heterogeneous Multilayer Structure

There are two techniques that can be used in performing heterogeneous multilayer structures: sprinkling modifier particles on the prepreg surface or premixing modifier particles with resin to be applied during the prepreg process. Consequently, a two step prepreg process was developed, referred to as double impregnation, which was utilized to develop a model multilayer prepreg. In this double pass impregnation, the modifier particles were premixed with the same matrix resin that was applied during the first pass impregnation step. The purpose of a conventional prepregging process is to impregnate collimated fiber tows with a desired amount of matrix resin at elevated temperature and pressure in order to create a uniform partially reacted lamina structure .Prepregging is a continuous process that consists of four basic operations. Firstly, the creation of the matrix resin film, then the coating, after that the impregnation zone where heat and pressure are applied to the ply and finally the prepreg, which is collected on a take-up reel. Modifier particles diameter is the factor that controls the amount of resin that will be applied during each impregnation step. The maximum diameter of the modifier particles can also be calculated, however more details on the calculation of the modifier particles' diameter are given in the autoclave process, which is one of the following units. During the second impregnation, the thickness of the resin film is equal to the average modifier particle diameter and thus, an almost monolayer particle distribution is obtained on the prepreg surfaces. Therefore, if the final prepreg fiber areal weight and resin content desired are known, the amount of resin that may be applied during the first impregnation can be calculated :

$$W_{r1st} = \frac{\left(\frac{A_f}{(1-W_r)} - A_f\right) - 2D_p p_r}{A_f + \left(\frac{A_f}{(1-W_r)} - A_f - 2D_p p_r\right)} \qquad (1)$$

Where

W_{r1st} = first pass weight fraction resin
W_r = final desired weight fraction resin
A_f = areal weight fibers [g/m2]
D_p = average diameter of modifier particles [m]
P_r = density of resin [g/m3]

2.1.2 Homogeneous Multilayer Structure

As far as the double pass impregnation in the homogeneous multilayer structure is concerned, a first pass resin starved step should be applied for pressing and packing the fiber bed. During the second pass of impregnation, the full thickness of the resin interlayer is applied creating a prepreg with an overall normal desired resin content. However, the application of the interlayer is not the same as in the heterogeneous structure. In the heterogeneous structure the modifier particles of both surfaces of two different laminas that come in touch are compressed and the final thickness of the multilayer laminate is equal to the diameter of modifier particles. On the contrary, in the homogeneous structure applying the second

step of impregnation under the same circumstances, more than the desired resin will be accumulated in the multilayer laminate.

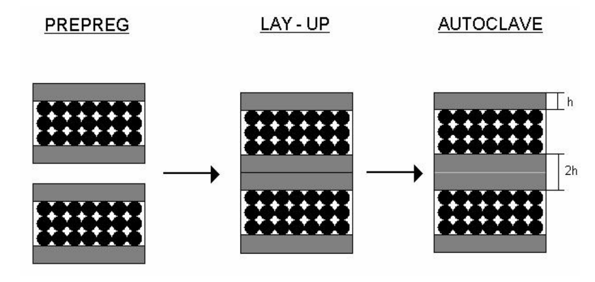


Figure 3: Second pass of impregnation

As it is obvious from Figure 3, if the full thickness is applied to both sides of the fiber bed, more resin than the desired one will be accumulated to the final matrix system. There are two possible different methods of applying the thickness interlayer and avoid accumulation of more than the desired resin. Firstly, by applying half the thickness of the resin in the second pass of the impregnation, a multilayer structure is achieved with the desired thickness of the interlayer without having more than the planned resin in the final matrix system. The second way of applying the interlayer is to enable it through one sided impregnation. This may complicate however the layup process. Both techniques are schematically shown in Figure 4.

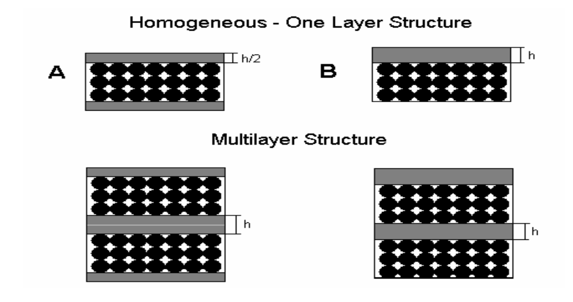


Figure 4: Two different ways for applying the homogeneous interlayer: (A)
Applying half the thickness of the resin in the second pass of the impregnation, (B)
Applying full the thickness of the resin only on one side of the fiber bed in them second pass of the impregnation.

The amount of resin that may be applied during each impregnation step will be controlled by the maximum thickness interlayer which is determined. Its determination however will be given in detail in the autoclave process which is one of the following units. If the final prepreg fiber areal weight and resin content desired are known, the amount of resin that may be applied during the first impregnation can be calculated by the formula (1) *(4)* if the D_p is replaced by the maximum thickness of the interlayer. Although heterogeneous multilayer structure can be used in composites in order to give a higher toughness between each ply, the homogeneous structure can be characterized not that efficient for the composites, as it only contributes to a thicker layer of resin between the plies. However, it can offer great toughness in hybrid materials, where a metal or other foil can be used instead of a single ply. The use of either a metal foil or any other non composite ply as a single ply to a composite material can be adjusted in a multilayer structure. Implementing the single layer to the impregnation process and setting the interlayer thickness, either half from both sides or full from one side is possible. The layered structure can be further processed by traditional layup and autoclave steps.

2.2 LAY – UP

Since both the impregnation passes have finished for all the plies the lay – up step follows, where the desired shape is given while the anisotropic nature of each ply is taken into consideration. During the lay – up process, prepreg tack is the overriding factor in prepreg performance. Prepreg must have the appropriate tack to stick each ply together, without being too much because the more tack a prepreg has the easier damage can be caused if a ply must be removed. Comparing the lay – up of a multilayer prepreg to a conventional one, a major difference can easily be observed as it is presented in Figure 2. In a conventional prepreg lay – up, only a small amount of resin will separate the two plies. On the contrary, the toughened prepreg lay – up will contain two full heterogeneous or two half homogeneous layers between each ply, one layer being supplied by each prepreg ply surface. The amount of resin located between plies will directly affect the resulting prepreg tack. It is important for the multilayer prepreg structure that resin is accumulated on the prepreg surface. If all the matrix resin has penetrated into the fiber bed, either modifier particles or nothing – depending if it is heterogeneous or homogeneous structure – will remain on the prepreg surface, which could create low tack prepreg.

2.3 AUTOCLAVE PROCESSING

The last step in composite manufacture is the autoclave process. During this step, heat and pressure are applied in order to cure the laminate with a homeomorphous fiber distribution. In the case of a multilayer structured composite, on how the autoclave process affect the resin distribution can be in detail described by Figure 2. The curing process of a conventional composite causes a flux of the resin, which develops a homeomorphous fiber with no distinct interface between the plies. On the contrary, the curing process of the multilayer composite although it also causes a flux of the resin, it forms distinct layers as the modifier particles in the heterogeneous case and the second resin film in the

homogeneous case are unable to penetrate into the fiber bed – due to the first pass impregnation – and they are trapped between each ply. Eventually, the morphology contains layers of reinforcing fibers embedded in a matrix resin separated by resin rich layers with a thickness that can be calculated. In the heterogeneous case, this interlayer contains twice the concentration of modifier particles that were initially placed on the prepreg surfaces. On the other hand, in the homogeneous case the desired resin is accumulated by placing only half of the resin thickness to each surface or full of it to one of the prepreg surfaces during the second impregnation step. At this point, it should be mentioned that there are limitations of the maximum thickness interlayer that can be used in processing. It is vital for the manufacture to be able to calculate the thickness of the interlayer so that the resin content in total remains constant as in a single pass of a conventional prepreg. The maximum thickness interlayer can be calculated as a function of the fiber areal weight, the final resin content and the maximum fiber packing arrangement. As the fiber packing becomes closer, the amount of resin required within each ply decreases and the amount of resin available for the interlaminar region increases. For the assumption that the maximum fiber packing arrangement is assumed to be between a square array and a hexagonal packed structure, as shown in Figure 5, the maximum thickness interlayer can be calculated:

$$T_1 = \frac{A_f\left(\left(1+\left(\frac{V_r}{V_f}\right)\right)\pi - 2(1+\cos(\theta))\right)}{p_f \pi} \qquad (2)$$

Where
A_f = fiber areal weight [g/m^2]
T_I = maximum thickness interlayer [m]
V_r = resin volume fraction
V_f = fibers volume fraction
p_f = fiber density [g/m^3]
θ = shift angle as defined in Figure 6 (for maximum effect θ = 30^o)

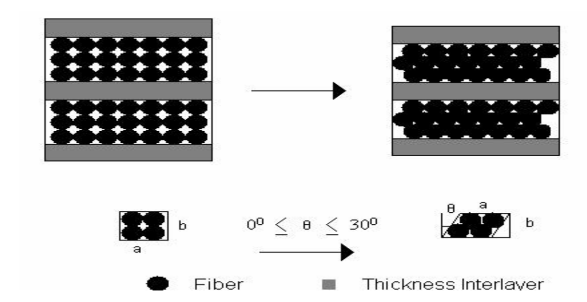


Figure5: Schematic of Fiber Packing Arrangements with the homogeneous interlayer implemented. Maximum packing achieved at θ = 30^o

As far as the heterogeneous case is concerned, the thickness TI can be replaced by the maximum modifier particles diameter D_{pmax}. Thus, the maximum modifier particles diameter that can be used in the interlayer is defined. As for the homogeneous case, the maximum thickness interlayer derives directly by formula (2)

3. EXPERIMENTAL

In order to investigate the role of the host resin matrix to the multilayer structure, three different model thermosetting resin systems were used in the present study.

• Firstly, an epoxy based resin system was tested which was composed by: 60% tetraglycidyldiaminodiphenylmethane (TGDDM) from Giba-Geigy as MY 720, 40% diglycidylether of bisphenol A (DGEBA) supplied by Shellas Epon 828, 10 parts per hundred parts epoxy (phr) polyethersulfone (PES) from Imperial Chemical Industries as Victrex 5003P and 42 phr diaminodiphenylsulfone (DDS) curing agent from Ciba-Geigy as HT 976 Hardener.

• Secondly, a dicyanate based resin system was tested which was composed by: AROCY M-20 dicyanate from Rhone – Poulenc polymers, 5% by weight P1800 polysulfone from AMOCO performance products and 2 phr REX 381 catalyst from Rhone – Poulenc polymers.

• Finally, the last model system was a bismaleimide (BMI) based resin system kerimid 70023 from Rhone – Poulenc. The epoxy, dicyanate and BMI resin systems were chosen due to the fact that they represent the temperature and the toughness capabilities for the most of the thermosetting resin systems. Typically, BMI is more brittle than epoxy which is more brittle than dicyanate. As far as the heterogeneous structure is concerned, in all resin systems, semi crystalline Nylon 6 particles from the Atochem Corporation were used as the modifier particles. The Nylon 6 modifier particles had an average particle diameter of 20 μm or 40 μm with product designations of Orgasol 1002 DNAT and Orgasol 1002 ES NAT respectively. The modifier particles were mixed with the base resin systems and applied during the impregnation processing. Concerning the homogeneous structure, the use of a homogeneous interlayer in order to lay up even plies of different material is under investigation.

3.1 PROCESSING

The prepreg samples during the process had a fiber areal weight of 255 g/m2 and final resin contents of 35% resin by weight. The reinforcing fibers of all the samples were Toray T800H 12K carbon fibers. The areal weights of the modifier particles that were applied during the second impregnation to

the prepreg surfaces were measured with an acetone extraction procedure. According to this procedure, the resin films produced during the second impregnation process were washed with acetone through a vacuum filtration apparatus. The base resin was soluble in the acetone and passed through the filter paper, while the modifier particles were not soluble in the acetone and was filtered out. Filter paper's weight increase was about to the weight of particles' which were applied to the prepreg surfaces. Then the modifier particle areal weight can be calculated by dividing it by the length and width of the resin film:

$$A_p = \frac{W_p}{L_f W_f} \quad (3)$$

Where:
A_p = modifier particle areal weight [g/m^2]
W_p = modifier particle weight in resin film [g]
L_f = resin film length [m]
W_f = resin film width [m]

3.2 FRACTURE TOUGHNESS TESTING

In order to perform the fracture toughness testing, a screw operated Instron mechanical testing machine, Model 4505, was used. Mode I interlaminar fracture toughness testing was attained by using Double Cantilever Beam (DCB) samples and Mode II interlaminar fracture toughness testing was attained by using End Notch Flexure (ENF) specimens. Both DCB and ENF samples are described in detail in Figure 6.

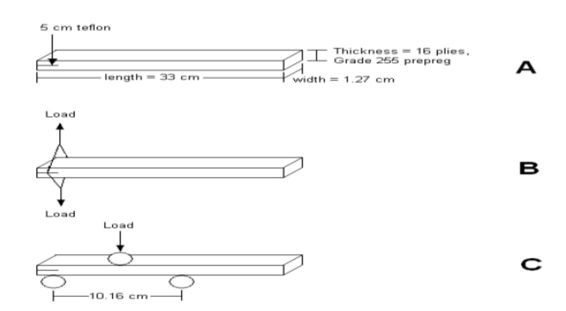


Figure 6: Fracture Toughness Configurations: A) Specimen dimensions, B) Double Cantilever Beam Testing and C) End Notch Flexure Testing *(5)*

The samples were made from 16 prepreg plies and with a 5 cm piece of Teflon inserted in one of the sample ends to serve as crack starter. DCB sample precrack was done in Mode I and ENF sample precrack was done in Mode II. More than 10 tests were performed for each DCB and ENF specimens. All ENF tests were done at a constant crack length of 2.54 cm and the DCB sample crack length was measured for each test.The Mode I fracture toughness was calculated with linear elastic fracture mechanics using an area method:

$$G_{1C} = \frac{\nabla A}{w \nabla a} \quad (4)$$

Where:
G_{IC} = Mode I critical strain energy release rate [J/m^2]
∇A =difference in area under adjacent load/displacement curves [J]
w = width of fracture sample [m]
∇a = increase in crack length [m]

The Mode II fracture toughness was calculated from elastic beam theory :

$$G_{IIC} = \frac{9a^2 P^2 C}{2w(3a^3 + 2L^3)} \quad (5)$$

Where:
G_{IIC} = Mode II energy release rate [J/m^2]
a = crack length [m]
P = maximum load [N]
C = sample compliance [Pa^{-1}]
w = sample width [m]
L = distance between central load and support [m]

4. RESULTS AND DISCUSSION

Figure7, presents the comparison of Mode I interlaminar fracture toughness between the dicyanate and epoxy model systems. The BMI model system G_{IC} results are not included due to a very high void content in the samples and poor fracture toughness results. The comparison of the epoxy structured laminates with the 0% modifier particles dicyanate system has a G_{IC} of 300J/m^2 compared to 550 J/m^2. After the creation of the multilayer structure, the dicyanate system shows a slight decrease in G_{IC} values similar to the results observed with the epoxy resin system. Furthermore, the dicyanate results show that the creation of the multilayer structure produces no improvement in the Mode I interlaminar fracture toughness.

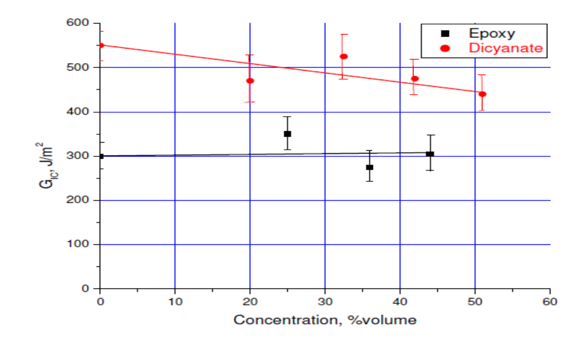


Figure7: Mode I Interlaminar Fracture Toughness (GIC) Comparison of Epoxy and Dicyanate Based Model Systems

as a function of Modifier Particle Concentration in Interlayer

Figure8, presents the comparison of Mode II interlaminar fracture toughness in the three model systems. Conventional structure laminate results demonstrate that the dicyanate is the toughest resin system and BMI is the most brittle with G_{IIC} unmodified values of 800, 500 and 250 J/m^2 dicyanate, epoxy and BMI respectively. All three systems show dramatic improvements in G_{IIC} with a maximum occurring for each system that shift towards higher concentrations as the host resin toughness increases.

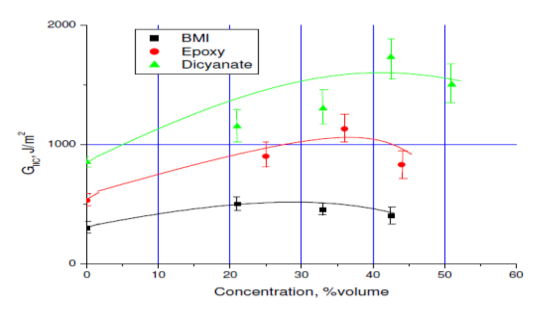


Figure 8: Mode II Interlaminar Toughness (G_{IIC}) Comparison of Epoxy, Dicyanate and BMI Based Model Systems as a function of Modifier Particle Concentration in Interlayer

The comparison of ENF results for the three model systems demonstrates that the host resin base toughness plays an important factor in the final layered structure toughness. Dicyanate, which is the toughest resin system, has the toughest multilayer laminate. BMI, which has the least tough resin system, has the least tough multilayer laminate. By plotting the ENF results as a percent G_{IIC} improvement in Figure 9, it is interesting to mention that all three systems present similar improvements in toughness. BMI produced a maximum improvement of 80%, epoxy produced an improvement of 118% and dicyanate produced a maximum improvement of 100%. BMI G_{IIC} improvement may be slightly low to some voids in the fracture samples.

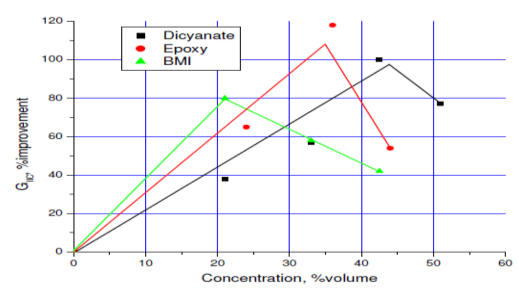


Figure 9: Percent Mode II Interlaminar Fracture Toughness Improvement of Epoxy, Dicyanate and BMI Model Systems as a function of Modifier Particle Concentration in Interlayer

Despite the fact that the toughness improvements of the three systems are similar, the maximums do not occur at the same modifier concentration levels. The BMI maximum occurs at 21% modifier particles, epoxy maximum occurs at 36% modifier particles and the dicyanate maximum occurs at 42% as presented in Figure 9. Consequently, the more brittle the resin system the lower the maximum concentration of modifier particles required to obtain similar toughness improvement. Observing the similar percent in G_{IIC} improvements for all host resin systems, it can be derived that there is a maximum ratio of interlaminar fracture toughness to intralaminar fracture toughness that cannot be exceeded. If the interlaminar fracture toughness is too high, crack propagation moves from a high toughness interlaminar region to a low toughness intralaminar region. Therefore, if the conventional Mode II fracture toughness of a thermosetting matrix composite is known, the maximum toughness capability of that system can be predicted by defining a toughness capability ratio:

$$T_C = \frac{G_{IICml}}{G_{IICcon}} = 2 \qquad (6)$$

Where:

T_c = toughness capability

G_{IICml} = maximum GIIC of multilayer laminate

G_{IICcon} = G_{IIC} of conventional laminate

This toughness capability of 2 may only be valid for the modifier particles used in this work. Higher toughness capability ratios may be obtained through the optimization of modifier particle shape, size distribution and interaction with the host resin matrix. Homogeneous multilayer structures have also to be tested and compared with the modifier particles results.

5. CONCLUSION

Concerning the toughness of the final multilayer laminate the host resin matrix is a major factor. The larger base resin toughness corresponds to the toughest final laminate. Nevertheless, the percentage increase of G_{IIC} due to the creation of the multilayer structure is relatively not dependent with the base resin toughness whose maximum toughness improvements corresponding to approximately 100%. Furthermore, the observed toughness improvements correlate directly to location of crack propagation during testing. If crack propagation occurs in the interlaminar region, toughness improvements can be expected. But if the crack moves into the intralaminar region, toughness can be degraded. The results of

the homogeneous multilayer structures are going to add more on this work and extend the existed conclusions. Understanding these fundamental differences in the level of process, structure and property between the multilayer and the conventional prepreg is essential for use in structural applications.

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